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X-RAY INVESTIGATION OF MOLTEN CRYSTAL HYDRATES $H_2SO_4 \cdot nH_2O$ AND $HNO_3 \cdot nH_2O$

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Voprosy Fiziki Metallov i Metallovedeni (Questions on the Physics of Metals
and Metallography), Academy of Sciences Ukrainian SSR, No. 4, 1953, pp 70-76



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X-RAY INVESTIGATION OF MOLTEN CRYSTALHYDRATES $\text{H}_2\text{SO}_4 \cdot n\text{H}_2\text{O}$ AND $\text{HNO}_3 \cdot n\text{H}_2\text{O}$

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Carried out in the present study is the X-ray investigation of the molten crystal hydrates $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ (84.5% H_2SO_4 by weight), $\text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$ (57.65% H_2SO_4 by weight), and $\text{HNO}_3 \cdot 3\text{H}_2\text{O}$ (53.8% HNO_3 by weight), using the method of integral analysis of the intensity curves. The procedure for obtaining the pictures is described in study [1].

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The diameters of the samples, for all of the investigated solutions, were selected as considerably less than the optimal diameters (diameters of 1.5 mm and 2.2 mm were selected for sulfuric acid, instead of 3.1 mm and 4.6 mm, and for nitric acid—a diameter of 3 mm instead of 12 mm); therefore, a correction for absorption was not introduced during calculation of the intensity curves.

Several samples were prepared from each of the solutions; two pictures were produced from each sample. The intensity curves for one and the same solution coincided, within the limits of measurement errors. Therefore, it was not necessary to resort to their averaging.

Results and Discussion

Shown in figures 1(a) and 2(a) are the intensity curves, adjusted to electron units for the liquids $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ and $\text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$.

Two maxima of intensity are revealed on the intensity curve of liquid $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$. The first corresponds to $\sin \theta / \lambda =$

*Numbers in the margin indicate pagination in the foreign text.

0.125, and the second—to $\sin \theta/\lambda \approx 0.44$.

The intensity curve which corresponds to the compound $\text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$ also has two maxima.

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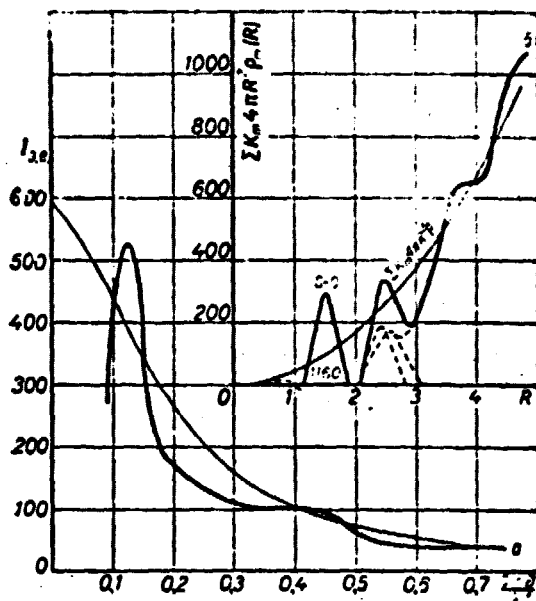


Fig. 1. Curve of intensity (a) and distribution (b) of liquid $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$.

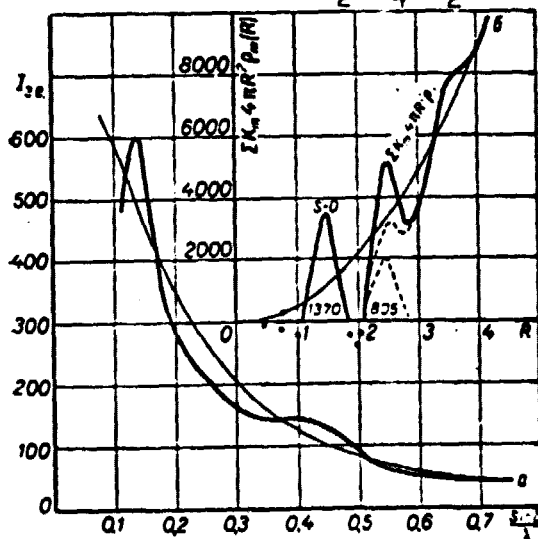


Fig. 2. Curve of intensity (a) and distribution (b) of liquid $\text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$.

Maximum II proves to be the same, in shape and position, /72
as in the case of $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$, and maximum I is displaced in
the direction of the larger angles. The curves in the area
of $\frac{\sin \theta}{\lambda} \approx 0.2-0.3$ differ appreciably from each other—a recti-
linear section is revealed in this area on the $\text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$
curve, and an interference maximum is clearly evident on the
X-ray photograph.

The increased intensity of the scattered radiation in
the area of $\frac{\sin \theta}{\lambda} \approx 0.2-0.3$ is naturally associated with
maximum II of water, which is localized with the same
 $\frac{\sin \theta}{\lambda}$.

Qualitative analysis of the curves makes it possible
to state that maximum II $\left(\frac{\sin \theta}{\lambda} \approx 0.44 \right)$ owes its origin to
structural formations, which do not change with concentration;
in the given case, it is with SO ions. The appreciable change
in the distribution of the intensity in the area of $\frac{\sin \theta}{\lambda}$ from
0.1 to 0.3, with a switch from $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ to $\text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$, is
due to substantial changes in the structure of the solution.

The function of distribution of electron density was
calculated according to the equation

$$\sum K_m \cdot 4\pi R^2 \rho_m(R) = \sum K_m \cdot 4\pi R^2 \rho_0 + \frac{2R}{\pi} \int_0^{\pi} S \left(\frac{I_{s,e} - \sum F_m^2}{F_s^2} \right) \sin(SR) dS,$$

where Σ designates the summation according to all the
atoms of the molecule;

K is the effective number of electrons of the atom m;

$F_m = \sum \frac{F_m}{\sum Z_m}$ is the scattering by one electron of the molecule;

$\sum Z_m$ is the number of electrons in the molecule;

R is the distance from a fixed atom;

$P_m(R)$ is the radial density of the electrons;

P_0 is the average density of the electrons in the solution;

$$S = 4\pi \frac{\sin \theta}{\lambda}$$

The average density of the electrons for the solutions was:

compound	$\rho \cdot \frac{1}{\text{\AA}^3}$
$\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$	0.554
$\text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$	0.472
$\text{HNO}_3 \cdot 3\text{H}_2\text{O}$	0.427

The data on the average effective numbers of electrons of the sulfur, oxygen, nitrogen, and hydrogen atoms are given below.

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compound	K_S	K_O	K_N	K_H	$\sum K_m$
$\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$	19.86	7.73	—	0.34	59.97
$\text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$	21.28	8.19	—	0.36	90.04
$\text{HNO}_3 \cdot 3\text{H}_2\text{O}$	—	8.65	7.62	0.37	62.11

The function of distribution of electron density for $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ is represented by the curve in figure 1(b), and that for $\text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$ by the curve in figure 2(b).

Observed on the curve of distribution of $\text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$ is

the single maximum I with $R = 1.5 \text{ \AA}$, and a clearly expressed maximum II with $R = 2.55 \text{ \AA}$, as well as a slight preference of the molecular distances in the liquid with $R = 3-4 \text{ \AA}$.

If one assumes that the position of maximum I ($R = 1.5 \text{ \AA}$) corresponds to the distance between the sulfur atoms and the oxygen atoms in the SO_4 ion, i.e., to the least possible distance, then the area beneath it should have been $2(K_s \cdot K_o) \cdot 4 = 1395$ units. The area was experimentally found to be 1370 units. This gives one the right to assume that maximum I corresponds to the interatomic distance S—O in SO_4^{--} , and is found to be in accordance with the data obtained during the investigation of the $\text{Na}_6(\text{SO}_4)_2\text{ClF}$ crystal.

Maximum II proves to be sufficiently acute, and corresponds to the distance $R = 2.55 \text{ \AA}$. It is close to the former in width. Therefore, it is natural to assume that it is associated with the preferential distances between the oxygen atoms in the SO_4 ion, on the one side, and with the adjacent water molecules on the other. The part of the area, caused by the intraion effect, is $(K_o \cdot 3K_o) \cdot 4 = 805$ units.

After subtraction from the total area of 2600 units of maximum II of the area, which corresponds to the O—O distance inside the SO_4^{--} (805 units), a maximum is retained on the curve, although it is not sharply pronounced (dotted II). The presence of the latter indicates that there is some preference in the mutual position between the oxygen atoms of the SO_4 ion and the water molecules. The fact that the position (with $R = 2.50-2.55 \text{ \AA}$) of the maximum nearly coincides with the distance between the oxygen atoms of the SO_4 ion and the nearest water molecules of a solid crystal hydrate of the same type as $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$ deserves attention [2].

Proceeding from the magnitude of the area of dotted

maximum II, one can calculate the number of water molecules N which "surround" each oxygen atom of the SO_4^{--} :

$$[2(K_o \cdot K_{H_2O})N] \cdot 4 = 1500 \text{ units:}$$

if one sets $K_o = 8.2$ and $K_{H_2O} = 10$, then it turns out that $N \approx 2.3$ molecules.

In solid $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$ crystal hydrate, each oxygen atom of the SO_4 ion is bonded with two water molecules. /74

We will note that the path of the distribution curve in the area from 1 to $3\text{\AA}$ corresponds well, as is shown above, to the tetrahedral model of the SO_4 ion, and completely precludes the possibility of a planar model. If the model of the SO_4^{--} were a planar quadrangle with oxygen atoms at the corners of the latter and a sulfur atom in the center, then there should be a maximum displayed on the distribution curve at $2.1\text{\AA}$. The experimental distribution curve at this point acquires a value equal to zero.

The distribution curve of $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ (fig. 1,b) also reveals two maxima: I—a single maximum with $R = 1.5\text{\AA}$, and II— $R = 2.55\text{\AA}$.

There is no doubt of the fact that maximum I characterizes the structure of the SO_4^{--} , just as in the case of $\text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$. Actually, the calculated area of the maximum $2(K_o \cdot K_s) \cdot 4 = 1235$ units, and the experimental area is 1160 units. The position of the maximum with $R = 1.5\text{\AA}$ corresponds to the S—O distance.

Just as in the case of $\text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$, maximum II is complex, corresponding to the preferential distance between the oxygen

atoms of the SO_4 atoms on the one side, and the oxygen atoms of the ion and the water molecules on the other.

Attention is drawn to the fact of the considerable decrease in the area of the second maximum and its great isolation, as compared with $\text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$, which is evidently found to be connected with the decrease in the percent content of water.

The area under the second maximum, with $R = 2.5 \text{ \AA}$, of the distribution curve is equal to 1600 units.

If, as in the preceding case, an area $(K_o \cdot 3K_o) \cdot 4 = 717$ units, which corresponds to the distance $R_{o-o} = 2.45 \text{ \AA}$ in the tetrahedral SO_4 ion, is picked out from the total area under the second maximum, then the number of water molecules bonded with each oxygen atom proves to be equal to ~ 1.3 molecules. There is no data on the structure of solid crystal hydrates of the same type at our disposal.

The intensity curve of the molten $\text{HNO}_3 \cdot 3\text{H}_2\text{O}$ crystal hydrate, and the distribution curve which corresponds to it, are given in figure 3 (a and b).

The single maximum I with $R = 1.2 \text{ \AA}$, and maximum II with $R = 2.10-2.15 \text{ \AA}$, are well expressed on the distribution curve of $\text{HNO}_3 \cdot 3\text{H}_2\text{O}$. In addition, with $R = 3.0-3.5 \text{ \AA}$, maximum III, which is weakly expressed, is also observed.

Maximum I on the distribution curve corresponds to the distance $R = 1.2 \text{ \AA}$. If one takes into account the fact that it is isolated, then it is natural to associate it with the intermolecular distance. In our case, this can only be the distance between the atoms in the complex NO_3 ion. If one proceeds from the known data on the radii of the nitrogen and

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oxygen atoms, given below, then $R = 1.2 \text{ \AA}$ should be considered the distance between the nitrogen and oxygen atoms in the NO_3 .

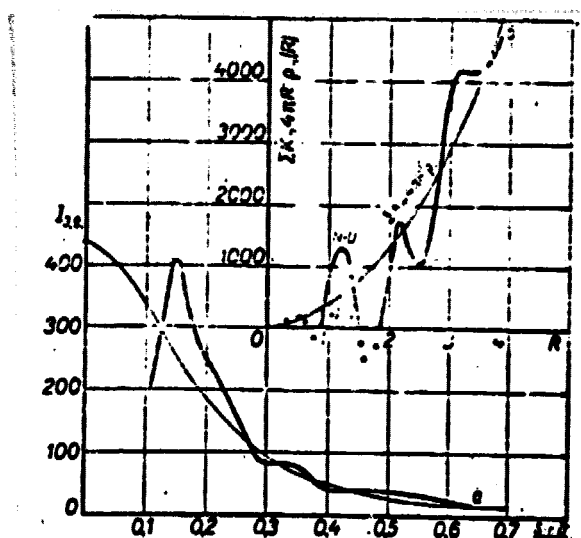


Fig. 3. Curve of intensity (a) and distribution (b) of liquid $\text{HNO}_3 \cdot 3\text{H}_2\text{O}$.

If one calculates the area which should be bounded by the curve in the area of maximum I, then, in this case, it should prove to be equal to $2(K_N \cdot K_O) \cdot 3 = 395$ units; in the experiment, a value of 420 units was obtained.

a. Атомы	b. Связи		
	c. одинарная	d. двойная	e. тройная
N	0.70	0.61	0.55
O	0.66	0.57	0.51

Key: a. Atoms d. double
 b. Bonds e. triple
 c. single

Thus, one can think that, in this interval of distances,

no other distances between the atoms, except R_{N-O} in the NO_3^- , occur.

The second maximum, located at $R = 2.10-2.15 \text{ \AA}$, is expressed sufficiently well, although it is not isolated. The area under it is equal to 700-730 units.

If one assumes that in the area R , encompassed by the second maximum, there occur distances between the oxygen atoms in the NO_3 ion, then, for the distances R_{O-O} , one should adopt $2.10-2.15 \text{ \AA}$. Judging by the nature of the curve, there are no distances less than $2.10-2.15 \text{ \AA}$.

In the literature, one can encounter two models of NO_3 : a planar model and a pyramidal model. In the first case, the oxygen atoms should be located at the corners of an equilateral triangle, and the nitrogen in the center of the triangle. Adopting the distance between the N and O as equal to $1.2 \text{ \AA}$, we obtain $2.07 \text{ \AA}$ for the R_{O-O} in the NO_3 . In the second case, the NO_3 ion is in the form of a pyramid, at the corners of the base of which are located the centers of the oxygen atoms, and at the apex—the nitrogen atom. /76

The position and relative magnitude of the area of the first and second maxima correspond well to the planar model, with parameters which coincide with those which were found for $NaNO_3$.

The distribution curve for the pyramidal model should differ substantially from that found experimentally.

Conclusions

X-ray investigation of molten crystal hydrates was carried out by the method of integral analysis of the intensity

curve.

Through consideration of the distribution curves of the electron density, it proved possible to draw the following conclusions on the structure of the complex SO and NO ions, and the short-range order in the structure of the solution.

1. Obtained by X-ray means were direct proofs that the SO_4 ion in the solution has a tetrahedral structure, with an $\text{S}-\text{O}$ distance equal to $1.5 \text{ \AA}$, while for the NO_3 in the solution, a planar triangular shape is probable, with an $\text{N}-\text{O}$ distance equal to $1.2 \text{ \AA}$.

2. The preferential distances between each of the oxygens of the SO ion and the nearest molecules of water proved near to the corresponding fixed distances in solid crystal hydrates. The average number of water molecules found at these distances is equal to ≈ 2.3 for an $\text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$ solution, and close to the coordination number in solid crystal hydrates, where it is equal to 2.

For an $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ solution, the average number of water molecules "surrounding" each oxygen atom of the SO_4^{--} is on the order of 1.3 molecules.

Hence, one can conclude that the preferential distances between the water molecules and the oxygen atoms of the SO ion, and the preference of their mutual position, correspond to the fixed position of these same elements of the structure in the solid crystal hydrate.

In conclusion, one should also note that the structure of the complex ions (SO_4 , NO_3) in liquid solutions is determined first by the interference method.

REFERENCES

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Sbornik nauchnykh rabot LMF AN USSR, No. 3 (1952).